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The program of 'Tractable High Performance Polymers' was an interdisciplinary research effort to develop the science and technology of synthesis, molecular characterization, processing and solid state characterization of novel tractable high performance rod-like polymers through different concepts of side group modification. Theoretical models for the mechanical behavior of oriented crystalline polymers and high-modulus polymers were developed. The influence of flexible alkyl side chains of rod-like polymers on the mechanical properties of highly oriented structures was theoretically analyzed and experimentally verified with poly(hexyl isocyanate). The role of hydrogen bonding in controlling the tensile deformation was investigated by solid state NMR. A variety of tractable para-linked aromatic LC polyesters, which were amorphous, were synthesized and fully characterized by several techniques. The tractability was achieved by the incorporation of novel aryl substituents and non-coplanar monomers into the chemical structure. These materials were processed from the liquid crystalline phase and then mechanically deformed through tensile processes. A large number of

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novel rod-like aromatic polyamides were synthesized using similar structural modifications with improved thermal and solubility properties. It was first demonstrated in this project that rod-like polyamides with non-coplanar units are lyotropic liquid crystalline. The improved tractability paves the way to new processing schemes for films, fibers and also blends of rods and flexible chain polymers.

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# **TRACTABLE HIGH-PERFORMANCE POLYMERS**

**Final Report**

**P. Smith, A. J. Heeger, D. Pearson and H.-W. Schmidt**

**November 1990**

**U. S. ARMY RESEARCH OFFICE  
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The program on '*Tractable High Performance Polymers*' was an interdisciplinary research effort to develop the science and technology of synthesis, molecular characterization, processing and solid state characterization of tractable high performance polymers. Two different approaches were developed; i.e. the synthesis of novel tractable high performance rod-like polymers through different concepts of side group modification, and an examination of the property potential of existing, common tractable polymers. The main achievements are outlined below.

- The molecular factors that limit the maximum achievable stiffness of tractable, conventional polymers, such as polyamides, polyesters, polyolefins, etc. were analyzed. Theoretical work revealed that the maximum degree of orientation, and therewith the maximum axial modulus, that can be achieved in tensile drawing of flexible chain molecules is dependent on the chain length of the polymer. It is predicted that the theoretical chain stiffness can be attained only at infinite tensile draw ratio. The finite chain length of processable macromolecules sets a limit, however, to the maximum draw ratio and scales as  $MW^{1/2}$ . These predictions were experimentally verified for poly(ethylene terephthalate), isotactic polypropylene, polyoxymethylene and poly(p-xylylene) that were oriented through tensile drawing. The limits to the axial tensile modulus, that can be achieved through tensile drawing, were calculated for these important polymers.

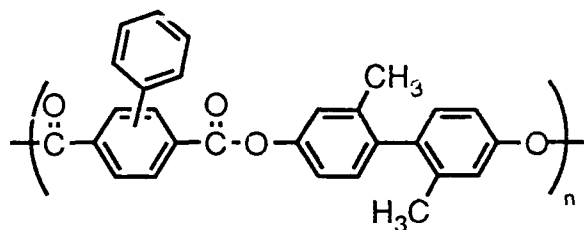
- The important factor for the deformation and the development of high performance *aliphatic and aromatic polyamides* is the better understanding of the role of the *hydrogen bonds* which govern the inter chain interactions. In order to address this issue the role of hydrogen bonding in controlling the tensile deformation behavior of nylon 66 is addressed. Solid-state nuclear magnetic resonance (NMR) experiments, on selectively deuterated samples, reveal that in the crystalline domains these secondary bonds are essentially static up to the melting temperature. The immobility, within the crystalline domains, of the hydrogen bonded amide groups gives rise to a maximum draw ratio which is essentially temperature independent and is far below that expected on the basis of molecular weight and flexibility considerations alone.

- A study was made of the effect of commonly used alkyl side chains for improved processability on the mechanical properties of highly oriented rigid chain polymers. We selected poly(*n*-hexyl)isocyanate (PHIC) as a model polymer, because of its well-known lyotropic behavior, simple synthesis and good solubility in many common solvents. PHIC is a polymer of the type  $-(NR-CO-)_n$  with  $R = n\text{-hexyl}$ . This polymer, of molecular weight of  $10^5$ , forms lyotropic phases in various solvents at concentrations exceeding 35 % v/v. In this work ultra-oriented monofilaments were prepared of this model polymer and their mechanical properties were measured and compared against those of high-strength/modulus poly(p-phenylene terephthalamide) (PPTA) and gel-spun ultra-high molecular weight polyethylene (UHMW PE) fibers. Experimental results obtained with ultra-oriented poly(hexyl)isocyanate fibers show that the side chains have a ruinous effect on the tensile modulus and stress at break. Simple calculations reveal that the theoretical modulus of rigid chain polyamides is reduced by about 90% by attaching *n*-hexyl side chains. This is due to reduction of the number of (uniaxially oriented) covalent bonds per unit cross-sectional area, and a weakening of secondary interactions. Major improvement of the mechanical properties is expected, of course, when after processing the solubilizing side groups are chemically or thermally removed and strong secondary bonds are restored. In the present case of polyisocyanates this may yield a route towards high-strength/modulus nylon-1 fibers. The mechanical properties can also be improved by increasing the modulus of the "solubilizing" matrix, for instance by cross-linking of the side chains or by improving the secondary interactions between side chains.

- Several structural modifications of *aromatic thermotropic polyesters* have been studied in this project in order to enhance the tractability and processing of this class of high performance polymers. A detailed study on the melt and solution properties of a substituted amorphous aromatic polyester by several characterization techniques has been completed. It was demonstrated that stiff, lateral substituents and the incorporation of noncoplanar 2,2'-disubstituted biphenylene moieties can be used effectively to improve the solubility, to reduce the crystallinity and to lower the melting temperature. In order to modify rod-like aromatic polycondensates novel temperature stable *biphenyl substituents* (4-biphenyl and 2-biphenyl) on terephthalic acid moieties were explored. The monosubstitution of poly-(p-phenylene terephthalate) with these

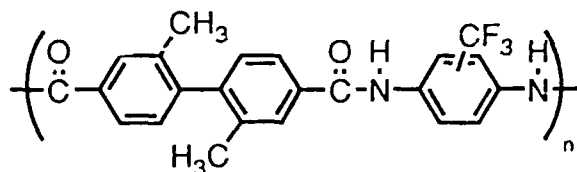
substituents resulted in polyesters with melting temperatures in the range of 285 °C - 350 °C.

As example polyester containing a non-coplanar biphenylene unit and a phenyl-substituted phenylene unit is a non-crystalline material with a glass transition temperature at 130 °C and a nematic phase up to decomposition temperature.

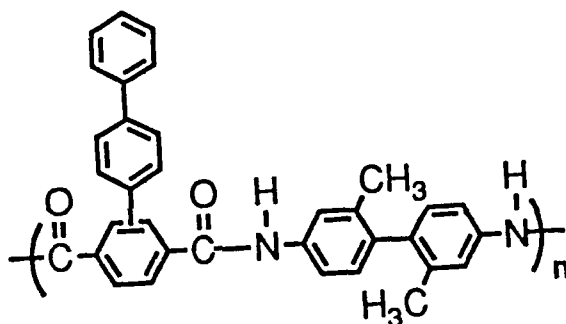


Various molecular weights of this material have been obtained through fractionation and rheological properties, thermal behavior, dilute and semidilute solution properties were examined. Particular the high molecular weight fractions have a strong tendency to form reversible gels even at low concentrations. The polyester was processed into fibers from isotropic solutions, gels and thermotropic melt. The best fiber properties were obtained from melt spun samples. This polyester could be drawn up to ten times leading to modulus in the range of 40 - 55 GPa. Generally crystalline LC-polyesters can not be drawn substantially. Our results demonstrate that with better tractable polyesters both processing from anisotropic melt and post drawing techniques can be applied and enhance the mechanical properties.

- A large number of *novel rod-like aromatic polyamides* were synthesized using similar structural modifications with improved thermal and solubility properties. Depending on the chemical structure, polyamides with very high solubility (up to 40% w/w) in polar aprotic solvents such as N,N-dimethylacetamide were obtained without the need for the addition of inorganic salts. Polyamide derived from a non-coplanar diacid and trifluoro-p-phenylene diamine is an example.



It was first demonstrated in this project that rod-like polyamides with non-coplanar units are lyotropic liquid crystalline. The improved tractability paves the way to new processing schemes for films, fibers and also blends of rods and flexible chain polymers. Several of these novel polyamides have been spun into fibers from isotropic and anisotropic solutions. For example the homopolyamid with a 4-biphenyl-substituent in the terephthalic acid unit and a non-coplanar diamin was processed from isotropic solutions in DMAc (14 % w/w).



The maximum draw ratio was found to be between 1.7 - 1.8 at 310 °C. This draw ratio is significant for rod-like aramids and demonstrates that the drawing behavior of these polymers can be improved by structural modifications.

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